Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gsrp20

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Published online: 22 Oct 2010.

To cite this article: Liqiang Wu , Xiaojuan Yang , Xiao Wang & Fulin Yan (2010): Cyanuric chloride-catalyzed synthesis of N-sulfonyl imines, Journal of Sulfur Chemistry, 31:6, 509-513

To link to this article: http://dx.doi.org/10.1080/17415993.2010.521940

Journal of Sulfur Chemistry
Vol. 31, No. 6, December 2010, 509–513

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Cyanuric chloride-catalyzed synthesis of *N*-sulfonyl imines

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(*Received 19 July 2010; final version received 4 September 2010*)

Cyanuric chloride is an inexpensive, efficient, and mild catalyst for the synthesis of *N*-sulfonyl imines by the reaction of sulfonamides with aryl aldehydes at 110 °C under solvent-free conditions. This method affords the *N*-sulfonyl imines in short reaction times, under solvent-free conditions, and in high yields.

Keywords: *N*-sulfonyl imines; sulfonamides; cyanuric chloride; solvent-free; synthesis

1. Introduction

N-Sulfonyl imines are versatile synthetic intermediates in organic synthesis (*1*, *2*). They are used in numerous reactions such as inverse electron-demand Diels–Alder reactions (*3–5*), in addition reactions as carbonyl equivalents (*6*), and in ene reactions (*7*, *8*). There are several methods available for the preparation of *N*-sulfonyl imines including the rearrangement of oxime *O*-sulfinates (*9*), Lewis acid- or solid acid-catalyzed reactions of sulfonamides with aldehydes or acetals (*10–21*), utilization of tellurium metal and chloramines T (*22*), halogen-mediated conversion of *N*-(trimethylsilyl) imines in the presence of the corresponding sulfonyl chloride (*23*), or two-step synthesis using sulfamic acid (*24*). However, many of the methods utilizing these reagents suffer from various drawbacks such as long reaction times, unsatisfactory yields, expensive and hazardous reagents, and cumbersome experimental conditions. Therefore, it seems highly desirable to find a simple and efficient protocol for synthesis of *N*-sulfonyl imines.

Cyanuric chloride (TCT, Figure 1), an inexpensive, easily available reagent of low toxicity and less corrosiveness than other similar reactants, has been widely used in organic reactions (*25–28*), but it has not been carefully studied as a catalyst in the synthesis of *N*-sulfonyl imines until now.

In continuation of our work to bring in and develop some new synthetic methodologies (*29–31*), we report that a new and simple TCT-promoted synthesis of *N*-sulfonyl imines by the reaction of sulfonamides with aryl aldehydes under mild conditions (Scheme 1).

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ISSN 1741-5993 print/ISSN 1741-6000 online

DOI: 10.1080/17415993.2010.521940
http://www.informaworld.com

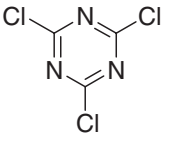
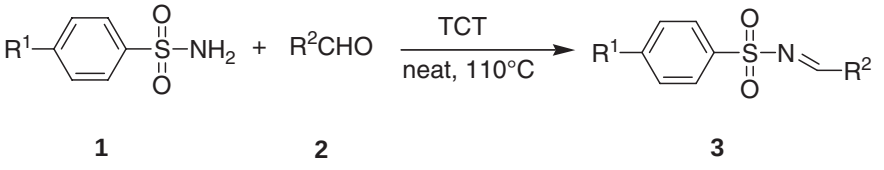


Figure 1. Structure of cyanuric chloride.



1 **2** **3**

Scheme 1. Cyanuric chloride-catalyzed synthesis of *N*-sulfonyl imines.

2. Results and discussion

In order to optimize the reaction conditions, we first examined the amount of catalyst and the reaction temperature, the reaction of benzenesulfonamide with benzaldehyde to the corresponding (*E*)-*N*-benzylidenebenzenesulfonamide was studied under solvent-free conditions in the presence of TCT at different temperatures. The results are summarized in Table 1. As shown in Table 1, the reaction using 15 mmol% TCT at 110 °C proceeded in highest yield.

With these results in hand, we turned our attention to the scope of the aromatic aldehydes in the reaction. The results are summarized in Table 2. Aromatic aldehydes containing electron-donating as well as electron-withdrawing groups smoothly underwent the conversion. The reaction proceeded at 110 °C within 3.5 h in excellent yields after the addition of the catalyst TCT (15 mol%) (Table 2). The structures of the products were established from their spectral properties (IR, ^{1}H-NMR, and elemental analysis) and also by comparison with the available literature data.

The plausible mechanism of the reaction is shown in Scheme 2. The adventitious moisture reacts with TCT to release 3 mol of HCl and cyanuric acid (removable by water washing) as a

Table 1. Synthesis of (*E*)-*N*-benzylidenebenzenesulfonamide under various conditions.[a]

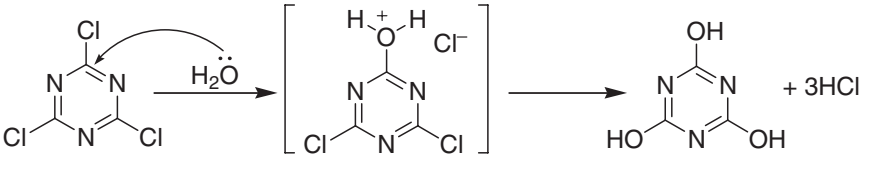
Entry	TCT (mol%)	Temperature (°C)	Time (h)	Yield (%)[b]
1	0	110	6	12
2	5	110	3	61
3	10	100	3	74
4	10	110	3	79
5	15	rt	6	49
6	15	50	6	62
7	15	90	4	71
8	15	100	2	89
9	15	110	2	93
10	15	120	2	92
11	15	130	2	90
12	20	100	2	88
13	20	110	2	90
14	25	110	2	87

Notes: [a]Reaction conditions: benzenesulfonamide (1 mmol); benzaldehyde (1 mmol); neat. [b]Isolated yield.

Table 2. Preparation of *N*-sulfonyl imines catalyzed by TCT.[a]

Entry	R^1	R^2	Time (h)	Product	Melting point (literature)	Yield (%)[b]
1	H	C_6H_5	2	**4a**	75–77 (77–78) (*17*)	90
2	H	4-Cl-C_6H_4	2.5	**4b**	132–133 (131–133) (*20*)	86
3	H	4-Br-C_6H_4	2.5	**4c**	204–205 (206–208) (*17*)	88
4	H	4-MeO-C_6H_4	2.5	**4d**	132–133 (130–132) (*17*)	82
5	H	4-Me-C_6H_4	3	**4e**	112–114 (114–116) (*20*)	85
6	H	3-NO_2-C_6H_4	3	**4f**	115–116 (113–114) (*15*)	79
7	H	4-NO_2-C_6H_4	3.5	**4g**	162–164 (161–163) (*17*)	75
8	H	2-F-C_6H_4	2.5	**4h**	121–124	82
9	H	2,4-Cl_2-C_6H_3	2	**4i**	121–122 (123–124) (*17*)	86
10	CH_3	C_6H_5	2	**4j**	109–110 (108–109) (*17*)	92
11	CH_3	4-Cl-C_6H_4	2	**4k**	169–170 (171–173) (*17*)	88
12	CH_3	4-MeO-C_6H_4	2	**4l**	125–126 (127–129) (*20*)	84
13	CH_3	4-Me-C_6H_4	2	**4m**	113–115 (112–114) (*17*)	82
14	CH_3	4-NO_2-C_6H_4	2.5	**4n**	159–160 (163–164) (*20*)	80
15	CH_3	2-Cl-C_6H_4	3	**4o**	128–130 (128–129) (*17*)	88
16	CH_3	2,5-MeO-C_6H_3	3.5	**4p**	122–123 (124–126) (*17*)	76
17	CH_3	2,4-Br-C_6H_3	3.5	**4q**	118–120	82
18	CH_3	2-Furyl	3	**4r**	99–100 (100–101) (*17*)	89
19	CH_3	3-Thiophenyl	3	**4s**	124–126 (127–129) (*17*)	92
20	CH_3	$CH_3(CH_2)_5CH_2$	2.5	**4t**	138–139 (136–137) (*20*)	80

Notes: [a]Reaction conditions: sulfonamide (1 mmol); aldehyde (1 mmol); TCT (0.15 mmol); 110 °C; neat. [b]Isolated yield.



Scheme 2. Proposed reaction pathway.

by-product. The *in situ*-generated HCl acts as a protic acid to activate the carbonyl oxygen to form the *N*-sulfonyl imines.

To recognize the capability of the present method in comparison with the reported methods for the preparation of *N*-sulfonyl imines from sulfonamides and aldehydes, the model reaction between benzenesulfonamide with benzaldehyde is described (Table 3). The results show that this method is superior to some previously reported methods in terms of yields and reaction times.

Table 3. Effect of catalyst on the reaction of benzenesulfonamide with benzaldehyde.

Entry	Reagent and conditions	Time (min)	Yield (%)	Reference
1	Silica chloride, solvent-free, 120 °C	180	75	(*10*)
2	$Si(OEt)_4$, 160 °C	360	68	(*11*)
3	$CaCO_3$, K10 Clay, $CH(OMe)_3$, microwave	6	69	(*12*)
4	$TiCl_4$, NEt_3, 0 °C, CH_2Cl_2	25	58	(*13*)
5	P_2O_5/SiO_2, solvent-free, 110 °C	120	88	(*14*)
6	ZrO_2, $S_2O_8^{2-}$, microwave	9	89	(*20*)
7	MgO, solvent-free, microwave	8	87	(*15*)
8	ZnO, solvent-free, 110 °C	240	90	(*16*)
9	TCT, solvent-free, 110 °C	120	90	This work

3. Conclusion

In summary, a new catalytic protocol to synthesize *N*-sulfonyl imines has been developed. Compared with previous reported methodologies, the present protocol features simple work-up, easy and quick isolation of the products, cheap and a catalytic amount of catalyst. This protocol avoids the use of hazardous solvent and toxic metallic catalysts and is of low cost.

4. Experimental

4.1. *General*

IR Spectra were determined on FTS-40 infrared spectrometer; NMR spectra were recorded on a Bruker AV-400 spectrometer at room temperature using TMS as an internal standard. Coupling constants (J) were measured in hertz; elemental analyses were performed by a Vario-III elemental analyzer; and melting points were determined on a XT-4 binocular microscope and were uncorrected. Commercially available reagents were used throughout without further purification unless otherwise stated.

4.2. *General procedure for the preparation of* N-*sulfonyl imines*

A mixture of the aldehyde (1 mmol), sulfonamide (1 mmol), and TCT (0.15 mmol) was stirred at 110 °C for appropriate time (Table 2). Completion of the reaction was monitored by thin layer chromatography. The material was cooled to 25 °C, and, after addition of water, the mixture was stirred for 5 min. The solid so obtained was filtered off and recrystallized from hexane–ethyl acetate mixture. The structure of the products was confirmed by NMR, IR, and comparison with authentic samples obtained commercially or prepared by reported methods. The spectral data of some new *N*-sulfonyl imines are given below.

(*E*)-*N*-(2-Fluoro-benzylidene)benzenesulfonamide (**4h**): White crystals, IR (KBr): υ 1648 (C = N), 1325 (S = O) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.41 (s, 1H), 8.08 (d, 1H, $J = 8.0$ Hz), 7.91 (d, 2H, $J = 8.4$ Hz), 7.60–7.48 (m, 3H), 7.35 (t, 2H, $J = 7.6$ Hz), 7.22 (t, 1H, $J = 7.6$ Hz); Anal. calcd for $C_{13}H_{10}FNO_2S$: C 59.30, H 3.83, N 5.32, S 12.18; found: C 59.42, H 3.90, N 5.26, S 12.09.

(*E*)-*N*-(2,4-Dibromobenzylidene)-4-methylbenzenesulfonamide (**4q**): White crystals, IR (KBr): υ 1652 (C = N), 1312 (S = O) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.42 (s, 1H), 8.10 (d, 1H, $J = 8.44$ Hz), 7.89 (d, 1H, $J = 8.0$ Hz), 7.46 (s, 1H), 7.40 (d, 2H, $J = 8.4$ Hz), 7.31 (d, 2H, $J = 8.0$ Hz), 2.44 (s, 3H); Anal. calcd for $C_{14}H_{11}Br_2NO_2S$: C 40.31, H 2.66, N 3.36, S 7.69; found: C 40.26, H 2.49, N 3.41, S 7.72.

Acknowledgement

We are pleased to acknowledge the financial support from Xinxiang Medical University.

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